

## Macroscopic models for water vapor and oxygen transmission in edible films

### Modelos macroscópicos para vapor d'água e transmissão de oxigênio em películas comestíveis

Antonio Carlos B. Antunes\*

Leila J. Antunes\*\*

Isa G. J. de Avellar\*\*\*

\* Instituto de Física, Universidade Federal do Rio de Janeiro.

e-mail: <antunes@if.ufrj.br>

\*\* Instituto de Engenharia Nuclear - CNEN.

e-mail: <leila@ien.gov.br>

\*\*\* Instituto de Química, Universidade de Brasília.

e-mail: <isaavl@unb.br>

#### Abstract

Some mathematical models to describe the water vapor permeability of edible materials are revised. In these macroscopic models, which are extensions of the linear diffusion model, the details of molecular phenomena are not considered. Gravitation drift effects, besides the diffusion flux observed in chocolate, are specifically considered. A diffusion plus adsorption model is proposed to describe the thickness effect on water vapor and oxygen permeabilities of hydrophilic films. The model is non-linear in the vapor or gas concentrations. A solution of the stationary diffusion plus adsorption differential equation is applied to transmission experiments of water vapor and oxygen through protein or polysaccharides based hydrophilic films. This model shows that adsorption is the main responsible for the thickness dependence of permeability in hydrophilic films.

**Key words:** Water vapor permeability. Moisture adsorption. Non-linear diffusion. Hydrophilic films. Thickness effect.

#### Resumo

Serão revisados alguns modelos matemáticos para descrever a permeabilidade do vapor d'água de películas comestíveis. Nestes modelos macroscópicos, os quais são extensões do modelo de difusão linear, os detalhes do fenômeno molecular não serão considerados. Efeitos de correntes gravitacionais, além do fluxo de difusão observado no chocolate, são especificamente considerados. Um modelo de difusão mais adsorção é proposto para descrever o efeito espesso na permeabilidade do vapor d'água e permeabilidade do oxigênio de películas hidrofílicas. Este modelo demonstra que adsorção é o principal responsável pela dependência de espessura nas películas hidrofílicas.

**Palavras-chave:** Permeabilidade do vapor d'água. Adsorção de umidade. Difusão não linear. Películas hidrofílicas. Efeito de espessura.

## 1 Introduction

The permeability of edible materials to water vapor is an important factor to be considered when choosing the covering and packing of food products. Experimental and theoretical methods have been developed to evaluate moisture transmission properties through edible films.

Two distinct experiments are usually employed to measure the physical magnitudes associated with permeability. One of them is a transmission experiment, identified as the cup method, performed according to the procedure prescribed by the ASTM (1980). The objective of this experiment is to measure the water vapor transmission rate (WVTR) through films. The experiment is performed by placing a testing film on the top of a cup filled with a desiccant to keep dry the air enclosed inside. The outer atmosphere is maintained at a constant concentration of water vapor. The gradient of humidity concentration established across the film produces a flux of moisture through the film according to Fick's law. The time evolution of the moisture transmitted through the film is measured by weighing the cup periodically.

Another method used to evaluate permeability properties is the absorption experiment (YOSHIDA; ANTUNES, A.C.B.; ANTUNES, A.J., 2002; YOSHIDA et al., 2003). In this experiment each sample of film, previously dried, is placed on an impermeable surface and exposed to an atmosphere of controlled humidity. Each film with its support is periodically weighed and the moisture absorbed is determined as a function of time.

Both experiments can be performed with an inversion of the boundary conditions. The transmission experiment can be inverted by placing the humid atmosphere inside the cup and the dry atmosphere outside, and the absorption experiment can be inverted by turning the plates supporting the films upside down.

Before elaborating physical models to describe the moisture flux in these experiments a qualitative analysis of the experimental data is put in order. After comparing the data obtained in the two opposed configurations in both experiments it is possible to evaluate if there are gravitational effects on the moisture flux or not.

Additionally, the time evolution of both the WVTR in the transmission and the moisture absorption experiments.

The absorption experiment may give some insights concerning the presence or absence of non-linear effects in the diffusion flux of moisture through the films. The absorption experiment is, at times, used solely to determine the boundary condition necessary to fit the data from the transmission experiment. In a previous paper (ANTUNES, A.C.B.; ANTUNES, L.J., 2000), we have shown that these experiments can be fitted independently with appropriate models.

Transmission and absorption experiments with chocolate were performed under several settings of humid atmospheres. Besides the vast application of chocolate in the covering of food products, it is also a good medium to illustrate water vapor permeability due to its complex composition of hydrophilic and hydrophobic constituents. This complexity gives rise to other effects concurrent with linear diffusion.

A critic observation of the data from an absorption experiment of water vapor in chocolate (ANTUNES, A.C.B.; ANTUNES, L.J., 2000) suggests the presence of non-linear effects. The time evolution of the mass of moisture absorbed reaches its maximum between 20 and 40 days, depending upon the humidity of the atmosphere. The decrease of the moisture absorbed after a maximum is a behavior that cannot be described by a linear diffusion model.

Another qualitative analysis of the experimental data gives significant information. It consists of comparing the WVTR in the two opposed configurations of the cup experiment. In the first configuration the air inside the cup is dried and the atmosphere above the film is humid. In the second configuration these conditions are inverted. The experimental data show that the WVTR in the first configuration is larger than that in the second one. This observation suggests that there exists a significant contribution of the gravitation drift on the moisture flux (ANTUNES; AVELLAR, 2003).

Permeability to water vapor and oxygen are important properties that determine the usefulness of hydrophilic films made with biopolymers such as proteins and polysaccharides. Should diffusion be the only property to contribute to water vapor and oxygen transmission across these films, and then permeability would be expected to be a characteristic of the material of the film, independently of the bulk of the matter. Measurements of the permeability of hydrophilic films, however, have shown results that depend on the thickness of the films (McHUGH; BUSTILLOS; KROCHTA, 1993; PARK; CHINNAN, 1995; CUQ, 1996).

Several arguments have been presented in the literature to explain this effect. Some authors propose that the swelling of the films during the vapor transmission may affect the measurement of permeability. Besides swelling, the polymer network in the film material would possibly be modified, leading to alterations in porosity and in consequence in permeability.

Another possible source of the observed thickness effect on water vapor permeability is attributed to features of the methodology for the determination of the permeability. In this experiment the film is placed over the open top of a cup containing a desiccant at its

bottom (ASTM, 1980; ANTUNES, 2003). Water vapor from the outer humid atmosphere crosses the film into the cup, is transmitted by diffusion through the stagnant air inside and finally is absorbed by the desiccant. When the system reaches the stationary state, the flux of vapor going into the film becomes constant. This is observed by periodically weighing the set (cup with film and desiccant), to determine the rate of moisture absorption. If the flux is large and the stagnant air inside the cup has not been completely dried, permeability evaluation could be masked by this effect (McHUGH; BUSTILLOS; KROCHTA, 1993).

Oxygen permeability is measured using other experimental conditions (ASTM, 2002). In this procedure, one side of the film is exposed to a pure oxygen atmosphere and on the other side a flow of pure nitrogen carries the oxygen that permeates through the film to a coulometric sensor that measures the flux of oxygen.

To describe the thickness effect observed in these measurements of permeability, a model in which the transmission property of the films is seen as an effect of two main phenomena, diffusion and adsorption, is here considered. In addition to diffusion, adsorption is supposed to be present as a result of the hydrophilicity of the biopolymers.

In the following sections we present two examples of mathematical macroscopic models that can describe these effects.

## 2 Diffusion Equation

According to the first Fick's law, the occurrence of a gradient of concentration of moisture in a permeable media produces a diffusion flux of moisture. This law is expressed by (CRANK, 1956):

$$J(x, t) = -D \frac{\partial}{\partial x} C(x, t) \quad (1)$$

where  $x$  is a variable that denotes the direction of the flux and  $t$  is time.  $C(x, t)$  is the concentration and  $J(x, t)$  is the flux of moisture. The factor  $D$  is the diffusion coefficient.

In the absence of sources and sinks of moisture the conservation of water in the permeable media is expressed by the continuity equation:

$$\frac{\partial C}{\partial t} + \frac{\partial J}{\partial x} = 0 \quad (2)$$

In cases in which the diffusion coefficient is a constant,  $D = D_0$ , equation (2) leads to a linear diffusion equation:

$$\frac{\partial C}{\partial t} - D_0 \frac{\partial^2 C}{\partial x^2} = 0 \quad (3)$$

In some media the interaction of the absorbed water with its hydrophilic components may produce variations in the diffusion coefficient. In these cases the diffusion coefficient is supposed to be a function of the concentration,  $D = D(C)$ . The diffusion equation for these cases is non-linear in the concentration:

$$\frac{\partial C}{\partial t} - \frac{\partial}{\partial x} \left( D(C) \frac{\partial C}{\partial x} \right) = 0 \quad (4)$$

If the non-linear effects are small deviations from the linear diffusion, the diffusion coefficient may be written as a linear correction of the constant  $D_0$  and reads:  $D(C) = D_0 + D_1 C$ , where  $D_1$  is constant (ANTUNES, A.C.B.; ANTUNES, L.J., 2000).

### 3 Solution of the Linear Diffusion Equation for Absorption Experiment

The material tested for moisture absorption was chocolate cut into disks with thickness  $L = 0.6$  mm and diameter  $d = 5.2$  cm. Each disk is placed on a horizontal and impermeable surface. The external surfaces are exposed to a controlled humid atmosphere. Due to the large diameter in comparison with the thickness,  $d \gg L$ , the flux of water vapour through the chocolate is one-dimensional and vertical. Likewise the flux, the variable  $x$  that denotes the direction of the flux is downwards oriented. The origin of  $x$ ,  $x = 0$ , corresponds to the external surface of the disk and the coordinate  $x = L$ , corresponds to the bottom of the slab.

In order to solve the diffusion equation, the initial moisture concentration in the chocolate disks and the boundary conditions must be established. The initial condition is the residual concentration of moisture in chocolate after drying the disks:

$$C(x, t = 0) = C_0 \quad (5)$$

The boundary condition on the external surface in contact with the humid atmosphere is established assuming, hypothetically, that it rapidly adsorbs water and becomes saturated. The concentration, then, remains constant:

$$C(x = 0, t) = C_a \quad (6)$$

At the bottom of the slab, which is in contact with the impermeable surface, there is no water vapor flux, a condition expressed by  $J(x=L, t) = 0$ .

Thus, according to the equation (1), the boundary condition on the concentration is:

$$\left. \frac{\partial C}{\partial x} (x, t) \right|_{x=L} = 0 \quad (7)$$

Then a solution of the linear diffusion equation (3) that satisfies these conditions can be obtained. That is a partial differential equation, with separable variables, which can be solved by the Fourier series method (YOSHIDA; ANTUNES, A.C.B.; ANTUNES, A.J., 2002; YOSHIDA et al., 2003; ANTUNES, A.C.B.; ANTUNES, L.J., 2000). The solution of the boundary value problem above is

$$C(x, t) = C_a - \frac{2(C_a - C_0)}{L} \sum_{n=0}^{\infty} \frac{\text{sen}(K_n x)}{K_n} \exp(-D_0 K_n^2 t) \quad (8)$$

$$\text{where } K_n = \frac{\pi}{2L} (2n + 1).$$

### 4 Differential Equation for Diffusion with Gravitation Drift

The flux of moisture through a permeable media is usually due to diffusion and described by Fick's first

law (CRANK, 1956). We assume that besides diffusion, there exists a second flux that is proportional to the concentration of moisture in the permeable media. With this assumption, the flux of moisture is supposed to be linear in the concentration.

In order to write the expression for this flux in one dimension, we denote by  $x$  the direction of the flux across a permeable slab. According to the above assumptions the one-dimensional flux is (ANTUNES; AVELLAR, 2003).

$$J(x, t) = -D \frac{\partial C(x, t)}{\partial x} + \alpha g C(x, t) \quad (9)$$

where  $C(x, t)$  is the concentration of moisture,  $D$  is the diffusion coefficient,  $g$  is the acceleration of gravity and  $\alpha$  is a parameter that measures the proportion of the gravitation drift in the flux. If there are no sources or sinks of water in the permeable media we can use the continuity equation

$$\frac{\partial C}{\partial t} + \frac{\partial J}{\partial x} = 0 \quad (10)$$

to obtain the differential equation for moisture concentration. Inserting the flux (9) in the equation (10) gives

$$\frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} + \alpha g \frac{\partial C}{\partial x} = 0 \quad (11)$$

This equation is linear in the concentration  $C(x, t)$  and can be solved exactly by the method of Fourier series (CRANK, 1956).

In some cases the free parameters of the model,  $D$  and  $\alpha$ , can be determined using solely a stationary solution. After a sufficiently long time of water vapor absorption, the concentration becomes time independent. In this stationary state, in which  $\frac{\partial C}{\partial t} = 0$ , equation (11) becomes

$$\frac{d^2 C}{dx^2} - \beta \frac{dC}{dx} = 0 \quad (12)$$

$$\text{where } \beta = \frac{\alpha g}{D}.$$

This equation corresponds to the configuration in which the flux is vertical and downward. It occurs when the humid atmosphere is above the film.

In the inverted configuration, the flux of moisture is upward and the corresponding equation can be obtained putting  $(-g)$  instead of  $g$ . Then, equation (12) becomes

$$\frac{d^2 C}{dx^2} + \beta \frac{dC}{dx} = 0 \quad (13)$$

### 5 Solution of the Stationary Equation for the Absorption Experiment

The solution of equation (12) is

$$C(x) = A + B e^{\beta x} \quad (13)$$

$A$  and  $B$  are arbitrary constants which can be determined imposing boundary conditions on the

concentration. For the absorption experiment in the configuration 1, in which the flux is downward, the boundary conditions are:

$$C(x = 0) = C_s \quad (15)$$

where  $C_s$  is the concentration of moisture at the external surface of the film in contact with the humid atmosphere. At the bottom of the slab, in contact with the impermeable surface, where there is no flux of moisture, the boundary condition is

$$J(x = L) = 0 \quad (16)$$

or

$$\left[ \frac{dC}{dx} - \beta C \right]_{x=L} = 0 \quad (17)$$

With the conditions (15) and (17), the solution (14) becomes (YOSHIDA et al., 2003)

$$C(x) = C_s e^{\beta x} \quad (18)$$

This is the spatial distribution of moisture concentration through the film in the stationary state. Letting  $S$  denote the area of the external surface of the film, the fraction of mass of moisture absorbed by the film in the configuration 1 is given by

$$M_1 = S \int_0^L C(x) dx = \frac{SC_s}{\beta} (e^{\beta L} - 1) \quad (19)$$

The corresponding results for configuration 2, in which the flux is upward, can be obtained putting  $(-\beta)$  instead of  $\beta$ :

$$M_2 = \frac{SC_s}{\beta} (1 - e^{-\beta L}) \quad (20)$$

From the results of the two configurations is obtained (YOSHIDA et al., 2003)

$$\beta = \frac{1}{L} \ln \left( \frac{M_1}{M_2} \right) \quad (21)$$

Thus, if in the two opposed absorption experiments  $M_1 > M_2$ , then  $\beta = \frac{\alpha g}{D} \neq 0$ , meaning that there is a gravitation drift flux of moisture, besides the diffusion flux.

## 6 Solution of the Stationary Equation for the Transmission Experiment

The stationary solution (14) of the differential equation (12) can be applied to the conditions of the transmission experiment performed using the cup method. The system under consideration is a slab of permeable edible material with thickness  $L$ . Equations (12) and (14) corresponds to configuration 1, in which the humid atmosphere is above the film and the dry air inside the cup is beneath the film. Under these conditions both the diffusion and the gravitation drift fluxes are downward. The boundary conditions are

$$C(x = 0) = C_s \quad \text{and} \quad C(x = L) = 0. \quad (22)$$

The arbitrary constants  $A$  and  $B$  of the solution (14) can be determined and the particular solution in which the configuration 1 becomes (ANTUNES; AVELLAR, 2003)

$$C_1(x) = C_s \left( e^{\beta x} - e^{\beta L} \right) / \left( 1 - e^{\beta L} \right) \quad (23)$$

The flux of moisture in the stationary state of configuration 1 is given by

$$J_1 = - D\beta C_s e^{\beta L} / \left( 1 - e^{\beta L} \right) \quad (24)$$

The flux in configuration 2, in which the boundary conditions are inverted, also needs to be determined. In this configuration the dried air is outside the cup, above the permeable film. The humid air, at controlled water vapor concentrations, is inside the cup, below the film. Under these conditions the diffusion flux of moisture is upwards and the gravitation drift flux remains downwards.

The differential equation (13), for the concentration in this configuration, has the stationary state solution

$$C(x) = A + B e^{-\beta x} \quad (25)$$

in which  $x$  is oriented upward. The respective boundary conditions are also

$$C(x = 0) = C_s \quad \text{and} \quad C(x = L) = 0. \quad (26)$$

The particular solution for this configuration is then

$$C_2(x) = C_s \left( e^{-\beta x} - e^{-\beta L} \right) / \left( 1 - e^{-\beta L} \right) \quad (27)$$

The corresponding stationary flux is

$$J_2 = - D\beta C_s e^{-\beta L} / \left( 1 - e^{-\beta L} \right). \quad (28)$$

If the moisture fluxes of the two configurations,  $J_1$  and  $J_2$ , are measured, the parameters of the model can be determined by

$$\beta = \frac{1}{L} \ln \left( \frac{J_1}{J_2} \right), \quad (29)$$

$$D = (J_1 - J_2) / \beta C_s \quad (30)$$

and

$$\alpha = \frac{\beta D}{g}, \quad (31)$$

where the concentration at the surface of the film,  $C_s$ , must also be determined experimentally.

After the determination of the two free parameters of the model,  $D$  and  $\alpha$ , contributions of the two fluxes can be evaluated and compared.

The mean flux through the film is given by

$$\langle J \rangle = \frac{1}{L} \int_0^L J(x) dx. \quad (32)$$

The mean values of the diffusion fluxes in these two configurations are

$$\langle J_{1,dif} \rangle = \langle J_{2,dif} \rangle = \frac{DC_s}{L} \quad (33)$$

For the gravitation drift fluxes we have (ANTUNES; AVELLAR, 2003):

$$\langle J_{1,gd} \rangle = \alpha g C_s \left[ \frac{1}{(1 - e^{-\beta L})} - \frac{1}{\beta L} \right] \quad (34)$$

and

$$\langle J_{2,gd} \rangle = \alpha g C_s \left[ \frac{1}{\beta L} - \frac{1}{(e^{\beta L} - 1)} \right] \quad (35)$$

## 7 Adsorption Model for Hydrophilic Films

Water vapor and oxygen permeabilities of biopolymer films are usually supposed to be governed by diffusion. The flux of vapor or gas is described by Fick's law (CRANK, 1956)

$$J(x,t) = -D \frac{\partial C}{\partial x}(x,t) \quad (36)$$

In this equation  $J$  is the flux,  $C$  is the concentration of vapor or gas,  $D$  is the diffusion coefficient,  $t$  is the time and  $x$  is a variable which denotes distances along the direction of the thickness of the film.

The space and time distribution of the concentration  $C(x,t)$  across the film is given by the diffusion equation

$$\frac{\partial C}{\partial t} + \frac{\partial J}{\partial x} = 0 \quad (37)$$

In order to describe the permeability of hydrophilic films we must modify this equation introducing a term that accounts for the possible adsorption of water or gas by the structural components of the film.

We assume that the amount of moisture absorbed depends on its concentration (CRANK, 1956). When the hydrophilic film is placed in contact with a humid atmosphere, the film surface rapidly reaches an equilibrium concentration of moisture,  $C_s$ , which will be called saturation concentration. This concentration  $C_s$  depends on the vapor transmission properties of the film and on the relative humidity of the environmental air.

The amount of vapor absorbed is proportional to the concentration fraction of vapor in the film, but it decreases when this concentration approaches the saturation concentration.

Taking into account both these effects, we assume that the amount of vapor absorbed is given by

$$S(x,t) = \lambda C(x,t) [C_s - C(x,t)] \quad (38)$$

Introducing this term negatively in the equation (37) we obtain

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \lambda C [C_s - C] \quad (39)$$

This partial differential equation is non-linear in the vapor concentration. It has the obstacles of non-linear equations: it is not separable in the variables and its solutions do not possess the superposition property (ANTUNES; A.C.B.; ANTUNES, L.J., 2000). These disadvantages can be circumvented linearising the equation. The adsorption term that is nonlinear can be approximated by a linear function. It can be observed that the function  $S$  defined in equation (38) vanishes for  $C = 0$  and  $C = C_s$ . Moreover, the maximum of adsorption occurs for  $C = C_s/2$ . These conditions can be satisfied by the linear function

$$A(x,t) = \begin{cases} \lambda \frac{2}{3} C_s C(x,t) \text{ for } C < C_s/2 \\ \lambda \frac{2}{3} C_s (C_s - C(x,t)) \text{ for } C > C_s/2 \end{cases} \quad (40)$$

With this adsorption term instead of  $S(x,t)$ , equation (39) becomes

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - A(x,t) \quad (41)$$

which is linear in  $C$ .

To show the significant effect of adsorption in permeability measurements, it is sufficient the stationary solution of equation (41), which corresponds to the condition  $\partial C / \partial t = 0$ .

Introducing the parameter  $K^2 = \frac{2\lambda C_s}{3D}$  and the stationary condition, equation (41) becomes

$$\frac{d^2 C}{dx^2} - K^2 C = 0 \quad (\text{for } C < C_s/2) \quad (42)$$

and

$$\frac{d^2 C}{dx^2} - K^2 (C_s - C) = 0 \quad (\text{for } C > C_s/2) \quad (43)$$

where  $C = C(x)$

The boundary conditions to be imposed on the function  $C(x)$  are given by the relative humidity of the air at both sides of the film.

The water vapor permeability of the film is measured performing the transmission experiment prescribed by ASTM (1980; ANTUNES, A.J., 2003), briefly described above. The film is mounted on top of a cup containing a desiccant, commonly silica gel, enclosing the air inside it. The desiccant dries the air inside the cup. The humidity of the external atmosphere is controlled and the external surface of the film in contact with the humid atmosphere remains at the saturation concentration  $C_s$ . The internal surface, in contact with the dry air, remains at null concentration. Thus the boundary conditions on the film concentration  $C(x)$  are

$$C(x=0) = C_s \quad \text{and} \quad C(x=L) = 0, \quad (44)$$

where  $L$  is the film thickness.

Due to these boundary conditions in the stationary regime of the water vapor flux, the concentration distribution has large values (near the saturation concentration) on half the film, where  $0 < x < L/2$ , and small values on the other half, where  $L/2 < x < L$ .

On the small values region,  $L/2 < x < L$ , the water vapor

concentration is ruled by equation (42). The solution of this equation that satisfies the boundary condition  $C(L)=0$  is

$$C_2(x) = A_2 \operatorname{senh}(K(L-x)), \quad (45)$$

where  $A_2$  is an arbitrary constant.

On the large values region,  $0 < x < L/2$ , equation (43) and the boundary condition  $C(0) = C_s$  give the water vapor concentration

$$C_1(x) = C_s - A_1 \operatorname{sen}(Kx), \quad (46)$$

with the arbitrary constant  $A_1$ .

The water vapor concentration  $C(x)$  and the flux  $J(x) = -D \frac{dC}{dx}(x)$  must be continuous at the middle plane  $x = L/2$ . So, it is necessary to impose on functions (45) and (46) the continuity conditions

$$C_1(x = L/2) = C_2(x = L/2)$$

and

$$C'_1(x = L/2) = C'_2(x = L/2) \quad (47)$$

With these two conditions, the two arbitrary constants  $A_1$  and  $A_2$  can be determined and the water vapor concentration is given by

$$C_1(x) = C_s \left\{ 1 - \frac{\operatorname{cosh}(KL/2) \operatorname{sen}(Kx)}{\Delta(KL)} \right\} \quad (48)$$

for  $0 < x < L/2$ , and

$$C_2(x) = C_s \frac{\operatorname{cos}(KL/2) \operatorname{senh}(K(L-x))}{\Delta(KL)} \quad (49)$$

for  $L/2 < x < L$ , where

$$\Delta(KL) = \operatorname{senh}\left(\frac{KL}{2}\right) \operatorname{cos}\left(\frac{KL}{2}\right) + \operatorname{cosh}\left(\frac{KL}{2}\right) \operatorname{sen}\left(\frac{KL}{2}\right)$$

From these functions the water vapor flux can be derived:

$$J_1(x) = DC_s K \frac{\operatorname{cosh}(KL/2) \operatorname{cos}(Kx)}{\Delta(KL)} \quad (50)$$

$$J_2(x) = DC_s K \frac{\operatorname{cos}(KL/2) \operatorname{cosh}(K(L-x))}{\Delta(KL)} \quad (51)$$

for  $0 < x < L/2$  and  $L/2 < x < L$  respectively:

The permeability  $P$  is related to the flux by the equation  $J = P \Delta p / L$  where  $L$  is the thickness of the film and  $\Delta p$  is the difference between the partial pressures of the vapor or gas on both sides of the film. Thus, measuring the magnitudes of  $L$ ,  $\Delta p$  and  $J$  the permeability can be calculated.

The water vapor permeability is measured by the cup method described in the introduction. The magnitude directly measured is the amount of moisture absorbed by the system made of film, stagnant air and desiccant, and is proportional to the flux of water vapor that enters the film. This flux is  $J_1(x=0)$ , obtained from equation (50). The thickness dependence of the water vapor permeability is given by

$$P_v(L) = \frac{LJ_1(0)}{\Delta p} = \frac{(DC_s/\Delta p)(KL)}{\left[ \operatorname{sen}\left(\frac{KL}{2}\right) + \operatorname{cos}\left(\frac{KL}{2}\right) \operatorname{tanh}\left(\frac{KL}{2}\right) \right]} \quad (52)$$

This is an increasing function of the thickness of the film.

The oxygen permeability is evaluated by the coulometer method which measures the amount of oxygen that outflows the film. This flux is  $J_2(x=L)$  which is given by equation (51). The oxygen permeability

$$P_o(L) = \frac{LJ_2(L)}{\Delta p} = \frac{(DC_s/\Delta p)(KL)}{\left[ \operatorname{senh}\left(\frac{KL}{2}\right) + \operatorname{cosh}\left(\frac{KL}{2}\right) \operatorname{tan}\left(\frac{KL}{2}\right) \right]} \quad (53)$$

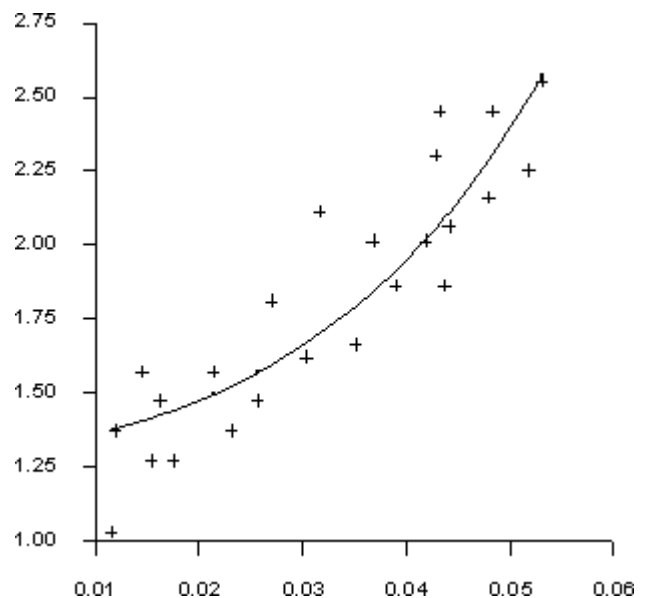
is a decreasing function of the thickness  $L$  of the film.

The fitting of the permeability functions (52) and (53) to the corresponding data allows the determination of the parameters  $A = DC_s/\Delta p$  and  $K$ . A good fit and a significant value of  $K$  attest the contribution of adsorption to the thickness effect.

## 8 Results and Discussion

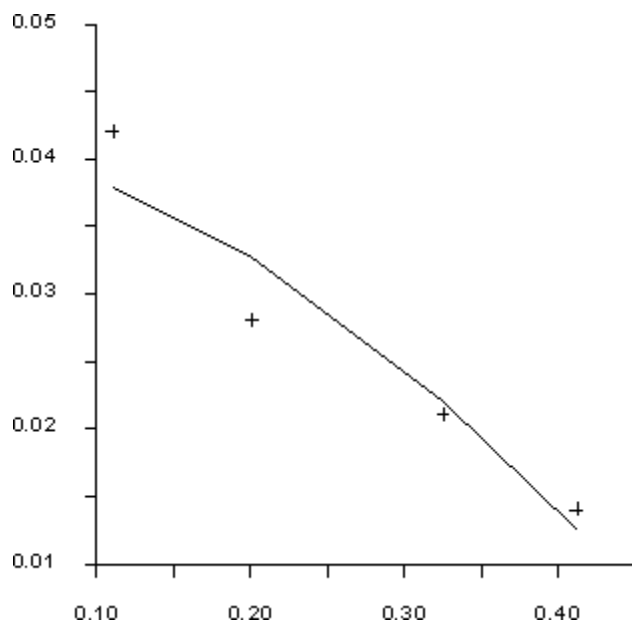
In order to determine the parameters of the model, equations (52) and (53) were fitted to published data for water vapor and oxygen permeability for several film thickness.

Fitting equation (52) to data of water vapor permeability for fish myofibrillar protein film in several film thickness (CUQ et al., 1996) gives  $K = 45 \text{ mm}^{-1}$ . The data and the fitted curve are shown in Graphic 1.



**Graphic 1.** The data points and the fitted curve for water vapor permeability  $P$  ( $\times 10^{12} \text{ mol m}^{-2} \text{ s Pa}$ ) as a function of the thickness  $L$  (mm) of fish myofibrillar protein films (CUQ et al., 1996).

Data for oxygen permeability of wheat gluten protein films (PARK; CHINNAN, 1995) are shown in Graphic 2. The value of the parameter  $K$  obtained by fitting the equation (53) to these data is  $6.2 \text{ mm}^{-1}$ . The fitted curve is also shown in Graphic 2.



**Graphic 2.** The data points and the fitted curve for oxygen permeability  $P$  ( $l\ m / m^2\ s\ Pa$ ) as a function of the thickness  $L$  ( $mm$ ) of wheat gluten protein films (PARK; CHINNAN, 1995).

The fitted curves presented in Graphics 1 and 2 show that the model describes the general features of the thickness dependence of the permeability.

It can be observed that the fitting of the parameters  $A=(DC_s/\Delta p)$  and  $K^2=(2\lambda C_s/3D)$  cannot determine the three parameters of the model:  $D$ ,  $\lambda$  and  $C_s$ . This is a consequence of the measurements done solely in the stationary regime of the experiment. To determine the three parameters, the fitting should be done with the time dependent solution of the diffusion-adsorption equation (41). Then, the flux of gas or vapor should be periodically measured along the time before the flux becomes stationary.

An alternative procedure is to perform an absorption experiment (YOSHIDA; ANTUNES, A.C.B.; ANTUNES, A.J., 2002; YOSHIDA et al., 2003; ANTUNES, A.C.B.; ANTUNES, L.J., 2000), which permits to determine the surface concentration  $C_s$  of vapor or gas on the film. The two experiments, done under the same environmental conditions, give the parameters of the model.

## 9 Conclusions

This non-linear model for diffusion and adsorption for water vapor and oxygen permeability in hydrophilic films shows that these are the main phenomena that account for transmission properties in films of this kind. Other effects may be present, although with minor contributions (ANTUNES; AVELLAR, 2003; HAGENMAIER; SHAW, 1990).

A more general result is that permeability, defined by  $P=LJ/\Delta p$ , is not a good parameter to compare transmission properties of films of different materials measured under different conditions and by different experiments.

If diffusion only were to contribute to permeability, then the transmission experiment would give  $P=DC_s/\Delta p$ , which is thickness independent. The adsorption, and possibly other effects, give rise to a thickness effect. This effect depends also on the experimental procedure to measure the flux  $J$ , as can be observed in the differences of thickness dependence for water vapor and oxygen transmission, given by equations (52) and (53).

The present model was fitted to the data using the computer code MINUIT (JAMES; ROOS, 1989).

## References

- ANTUNES, A. C. B.; ANTUNES, L. J. Non-linear effects in moisture adsorption by chocolate. *International Journal of Food Science and Technology*, Oxford, v. 35, n. 3, p. 323-329, 2000.
- ANTUNES, A. C. B.; AVELLAR, I. G. J. Water vapour transmission in chocolate. *International Journal of Food Science and Technology*, Oxford, v. 38, n. 4, p. 493-497, 2003.
- ANTUNES, A.J. *Funcionalidade de proteínas de soro de leite bovino*. São Paulo: Manole, 2003.
- ASTM. Standard test methods for water vapor transmission of materials. In: ASTM Book of Standards. West Conshohocken, PA: American Society for Testing and Materials, 1980. p. E96-80.
- ASTM. Standard test methods for oxygen gas transmission rate through plastic film and sheeting using coulometric sensor. In: ASTM Book of Standards. Designation: D3985-02. West Conshohocken, PA: American Society for Testing and Materials, 2002. p. 656-661.
- CRANK, J. *The mathematics of diffusion*. Oxford: Clarendon Press, 1956.
- CUQ, B. et al. Functional properties of myofibrillar protein based biopackaging as affected by film thickness. *Journal of Food Science*, Chicago, v. 61, n.3, p. 580-584, 1996.
- HAGENMAIER, R.D.; SHAW, P. E. Moisture permeability of edible films made with fatty acid and (Hydroxypropyl) methylcellulose. *Journal of Agricultural and Food Chemistry*, Washington, v. 38, n. 9, p. 1799-1803, 1990.
- JAMES, F.; ROOS, M. *MINUIT, function minimization and error analysis*. CERN 0506, Geneva, Switzerland: CERN Program Library Office (1989).
- McHUGH, T. H.; BUSTILLOS, R. A.; KROCHTA, J.M. Hydrophilic edible films: modified procedure for water vapor permeability and explanation of thickness effect. *Journal of Food Science*, Chicago, v. 58, n. 4, p. 899-903, 1993.
- PARK, H. J.; CHINNAN, M. S. Gas and water vapor barrier properties of edible films from protein and cellulosic materials. *Journal of Food Engineering*, Oxford, v. 25, n. 4, p. 497-507, 1995.

YOSHIDA, C. M. P.; ANTUNES, A. C. B.; ANTUNES, A. J. Moisture adsorption by milk whey protein films. *International Journal of Food Science and Technology*, Oxford, v. 37, n. 3, p. 329-332, 2002.

YOSHIDA, C. M. P. et al. An analysis of water vapour diffusion in whey protein films. *International Journal of Food Science and Technology*, Oxford, v. 38, n. 5, p. 595-601, 2003.